Title: Profiles of $\partial^{13}C$ and ∂D in Methane from the Lower Stratosphere

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Methane is an important green house gas of biogenic and anthropogenic origin for which global budgets are being constructed from a variety of data. One approach to a global methane budget is the use of the stable isotopes ^{13}C and D, and the radionuclide ^{14}C as tracers (1). We measured the isotopic composition of methane from various sources and in tropospheric air for a number of locations. Here we report on the isotopic composition of methane collected from the lower stratosphere. As in the troposphere, the main sink for methane in the lower stratosphere is the oxidation by OH radical; higher up oxidation by O^1D and Cl become increasingly important. Measurements of the isotopic methane composition in the stratosphere can yield estimates for the kinetic isotope effects in the methane destruction reactions. These effects have to be known for quantitative isotopic methane budgets.

Large air samples were collected from the lower stratosphere (tropopause to about 19 km altitude, in mid and low latitudes of the northern hemisphere) aboard the NASA WB-F57 airplane with a compressor system similar to those we use to collect samples from sources and tropospheric air. Compatibility of the airborne collection system for CH_4 and N_2O concentrations and isotopic methane composition measurements was established by ground tests using both sampling systems simultaneously. The samples were processed and measured identical to the procedures described in (1). The radionuclide ^{85}Kr was also measured in these samples.

The observed CH_4 and N_2O concentrations decrease with altitude, and the profiles for different latitudes look similar to those obtained by others. The profiles become most coherent when concentrations are plotted against altitude above the local tropopause heights, which were obtained by interpolating sounding data from weather stations along the flight path. The concentrations of CH_4 and N_2O linearly correlate with a slope characteristic for the lower stratosphere. As N_2O concentrations drop faster relative to CH_4 concentrations higher up in the stratosphere, complications by subsiding air can be excluded in our data set.

The methane $\delta^{13}C$ and δD values become significantly and successively enriched with increasing altitude and decreasing CH_4 concentration when compared to the tropospheric values. This behavior is attributed to the effect of isotopic fractionation occuring in the destruction reactions. The kinetic isotope effect α is the ratio of the reaction rate constants for two isotopically different molecules, and $(\alpha - 1) \times 1000$ is the enrichment factor ϵ for a reaction. In a

simple steady state 1-box approach the factor is also
$\epsilon = \Delta \delta / \ln(CH_{4\ local}/CH_{4 troposphere})$, i. e. the ratio of the change in isotopic composition to the natural logarithm of the fraction of CH_4 surviving the destruction, and thus given by the slope in the profiles shown below.

More detailed chemical models will be presented and discussed to deduce estimates for the enrichment factors of ^{13}C and D of CH_4 in the OH destruction reaction. The model considers transport by using the measured ^{85}Kr concentrations which indicate the age of the air as function of altitude (time since it left the troposphere). The obtained results will be compared to existing ones from laboratory experiments (for ^{13}C), and the implications for methane budget calculations will discussed.
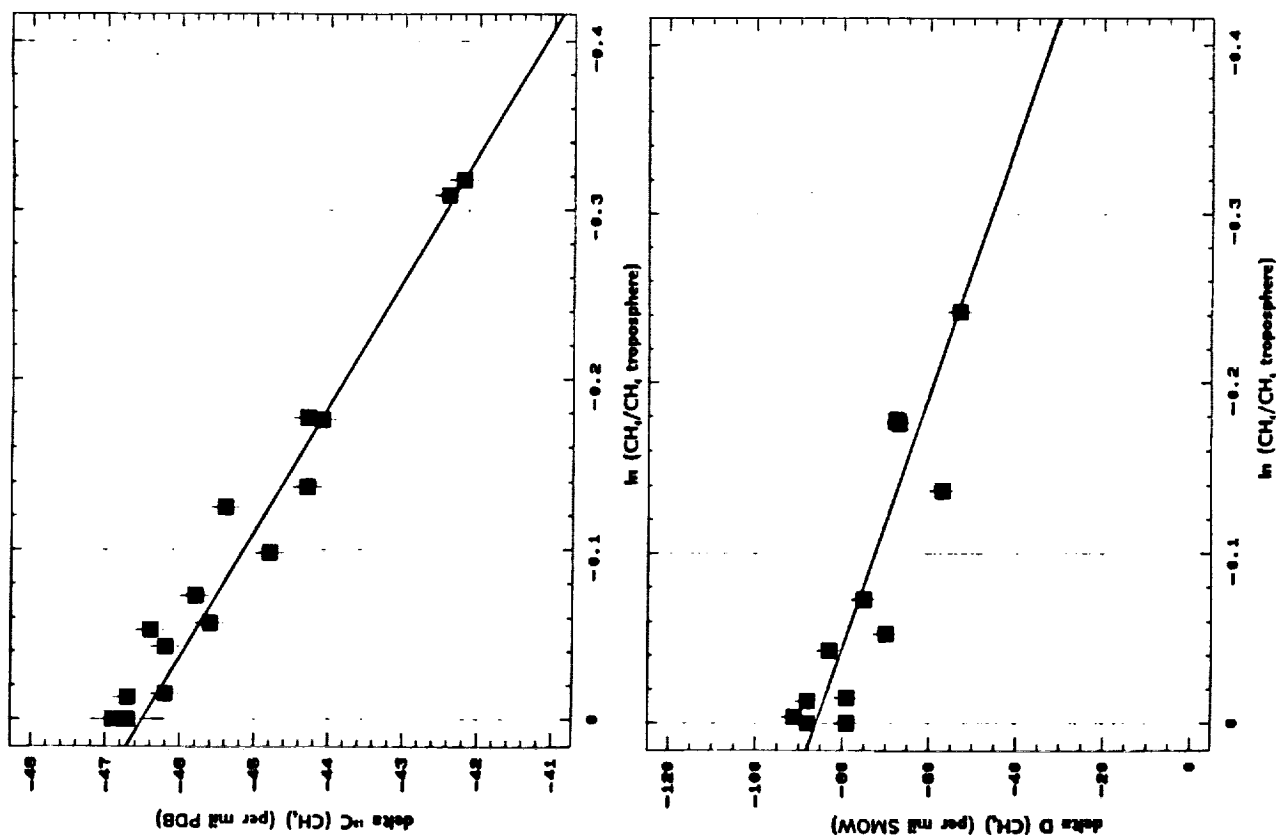
Ref.: (1) M. Wahlen et al., Science 245 (1989) 286.